INTERPRETING RAPID COAL DEVOLATILIZATION AS AN EQUILIBRIUM FLASH DISTILLATION DRIVEN BY COMPETITIVE CHEMICAL KINETICS

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Introduction

As the ambient pressure for a coal devolatilization process is reduced, ultimate yields of tar increase substantially. For high volatile bituminous coals, tar yields from vacuum pyrolysis can be fifty percent greater than from high-pressure pyrolysis. This behavior has long been attributed to competitive secondary chemistry in the gas phase occurring on a time scale dictated by transport of volatile matter through the particle surface. Among the escape mechanisms compatible with coal's complex physical structure, bulk and Knudsen pore diffusion, external film diffusion, continuum flow, and bubble growth in viscous melts have been treated, as reviewed recently by Suuberg (1).

These models correlate the reduced ultimate yield for increased ambient pressures, but important features of pyrolysis over a range of pressure remain unexplained. First, the measured rate of weight loss for identical thermal histories is the same for pressures between vacuum and 3.45 M Pa (2). Second, tar deposition exerts a negligible influence on both yields and evolution rates throughout all pressures of practical interest, based on the scaling from an independently-measured tar cracking rate and a measured volatiles escape rate (3). Third, the molecular weight distributions (MWD) of tar shift toward lower molecular weights as the ambient pressure is increased (1,4,5).

The reaction model introduced here (FLASHKIN) correlates the reduced ultimate yields, predicts evolution rates which are independent of pressure, and explains the observed shifts in tar MWD for varied ambient pressures. It interprets coal devolatilization as a single-stage equilibrium flash distillation driven by competitive chemical kinetics. While the mathematical formulation accommodates rate-limiting mass transport resistances, homogeneous chemistry is excluded and mass transport resistances are deemed negligible for the particle sizes considered in the comparisons with data. In this respect, FLASHKIN advances a minority viewpoint rooted in the parallels between pyrolysis and evaporative drying drawn by Peters and Bertling (6), and the aspects of phase equilibrium included in the models of James and Mills (7) and Niksa (8).

Reaction Mechanisms

The reaction mechanisms in FLASHKIN develop an analogy between coal pyrolysis and a single-stage equilibrium flash distillation. In any flash distillation, an equilibrium relation (such as Raoult's law in the simplest case) describes the partitioning of chemical species into the vapor and condensed phases at fixed pressure and temperature. The portion of the feedstream which evaporates is determined by a mole balance among the feed and product streams. Usually the composition and throughput of the feedstream and the temperature and pressure of the flash chamber are known, so that the composition and efflux of the vapor and liquid streams can be determined.

In the coal pyrolysis reaction system, there is no feedstream per se; rather, the coal macromolecule disintegrates into fragments which range in size from hydrocarbon gases having an average molecular weight of 25 g/mole to polymeric pieces of coal of molecular weight to, perhaps, 10^4-10^6 g/mole. The rate at which theses species are introduced into the system is determined by the primary thermal reactions.

The flash chamber is, of course, the porous fuel particle. In softening coals, the vapor is fully dispersed throughout the melt as bubbles in a viscous liquid; otherwise, the vapor is dispersed throughout a pore system which delineates solid subunits of a few hundred angstroms in size (the size of mesopores). Regardless of the form of the condensed phase, we assume that their composition is uniform throughout the particle, because the characteristic dimension of the subunits of condensed matter is so small. The temperature of the system is externally imposed and, under the restriction of negligible internal heat transfer resistances, the particle is isothermal. But the internal pressure reflects the reaction dynamics. In actuality, the internal pressure reaches a level compatible with the generation rate of gases and the resistance to escape. Despite the modeling discussed earlier, the internal pressure remains ambiguous because coal's physical structure admits several plausible transport mechanisms, and also because the transport coefficients are uncertain. We assert that the time scale for mass transport is much shorter than the primary decomposition time, as applicable to continuum flow driven by a pressure gradient, and deduce that the internal and ambient pressures are nearly equivalent.

Since the primary decomposition fragments encompass light gases and high polymers, the vapor is regarded as a binary mixture of (a) noncondensibles, restricted to molecular weights below 100 to represent light gases, and (b) a continuous mixture of vapor fragments of molecular weight from 100 to infinity, to represent tar. The tar vapor is represented by a continuous MWD. The condensed phase is envisioned as a binary mixture of nonvolatile char and a continuous mixture of evaporating compounds of molecular weight greater than 100; again, the condensed-phase continuous mixture is represented by a continuous MWD.

Equilibrium is asserted between the vapor and condensed continuous mixtures on the basis of scaling the molar concentrations in the vapor and condensed phases. Since the densities of gaseous and condensed species differ by three to four orders of magnitude, the accumulation of vapor within the particle is entirely negligible. In other words, the vapor composition is in quasi-steady equilibrium with the changing condensed phase composition. The time scale on which the phase equilibrium is established is the shortest in the system.

The compositions of the continuous mixtures in the vapor and condensed phases are related by a generalization of Raoult's law. This simple form is in keeping with the lack of data on high molecular weight coal products such as tar. Nevertheless, the formulation in FLASHKIN is more advanced than previous renderings of Raoult's law in pyrolysis modeling (7-9).

Until very recently, multi-component phase equilibrium was analyzed in terms of discrete pseudo-components presuming that basic thermodynamic relations expressed in terms of the mole fractions of the species apply, computational burdens notwithstanding. Their obvious limitation is that discrete mole fractions for mixtures as complex as coal tar are impossible to measure. "Continuous thermodynamics" circumvents this deficiency by recasting the conditions for phase equilibria in terms of continuous distributions of macroscopic characteristics such as aromaticity, carbon number, normal boiling point and, most pertinent to this model, molecular weight. Recent publications by Prausnitz and coworkers (10,11) and Ratzsch and Kehlen (12) develop the results used in FLASHKIN and access the literature on the general theory.

Finally, to complete the analogy between pyrolysis and a flash distillation, the efflux of vapor and liquid "products" must be specified. The efflux of vapor species is simply the sum of the evolution rates of gas and tar. Within the constraints of negligible mass transport restrictions and negligible vapor accumulation noted above, the escape rate of light gases must match the generation rate of gases from the primary thermal reactions; i. e., gases escape at their rate of production by chemical reaction. The tar evolution rate is also specified by this rate, with the additional constraints that mole fractions for the binary vapor sum to unity, and that phase equilibrium is maintained.

Of course, no condensed phase species leave the particle. But their efflux rate is analogous to the rate at which the condensed continuous mixture forms an involatile char. Lacking guidance from experiment, we assume that the char formation rate is independent of the molecular weight of the components in the mixture.

The basic structure of coal pyrolysis, especially tar evolution, shares many similarities with a single stage equilibrium flash distillation. The amount of tar in the vapor phase within the fuel particle is in equilibrium with a continuous mixture of high molecular weight fragments in either the solid subunits or viscous melt. Generation rates and the efflux of intermediates and products are established by chemical reaction rates. As elaborated in the full paper, the evolution rates of tar and light gases, and the tar MWD are completely specified by closing the mole balance among the reaction species.

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